STATUS REPORT
ON
RESEARCH ON THE ELECTRICAL PROPERTIES
OF
SEMI-CONDUCTORS

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Approved by:

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1. INTRODUCTION

1.1 Purpose

This is the fifth status report on the lead telluride investigation being carried out under ONR sponsorship at the University of Illinois. This report covers the period 1 September to 30 November 1953. The purpose of the investigation is to study the semi-conducting properties of PbTe single crystals of various compositions. Seven additional samples have been produced and some progress has been made in attempting to find ways of controlling the composition of the crystals.

1.2 Personnel

As reported previously, Mr. Oleg Golubjatnikov, a graduate student working on half-time appointment, and Mr. Richard T. Pfluger, an undergraduate working by the hour, joined the project in September. Mr. Golubjatnikov has calibrated the electromagnet and has carried out a number of routine resistivity measurements on the PbTe samples. Mr. Sirrine has devoted his attention to the problem of growing the crystals. Most of the improvements in apparatus and technique were suggested by him. Mr. Pfluger has worked on a number of necessary odd jobs on the project, and has taken over some of the more routine tellurium purification work.

2. EQUIPMENT AND FACILITIES

No major items of equipment have been added during the period covered by this report, but a number of revisions of existing equipment were made. The tellurium fractional sublimation apparatus was redesigned to eliminate all rubber hoses and stoppers to guard against the introduction of impurities. The mixing apparatus was redesigned to permit sealing off the crucible under a pressure of hydrogen rather than a vacuum, if desired. The Stockbarger furnace has been modified to permit different dropping rates. A more effective method of continuous control is being worked out.

3. SUMMARY OF ACTIVITIES

3.1 Zone Purification

Zone melting was tried on a polycrystalline boule of PbTe to get some idea of the power requirements and the sensitivity of controls needed. A quartz crucible was suspended in a vertical position and the RF coil, consisting of a single turn of copper tubing carrying cooling water, was manually moved up and down. An induction heater in the Electron Tube Laboratory was found to have sufficient power, and can be used as needed in the future. Further experiments along these lines were deferred until the crystal growing procedures are better in hand.

3.2 Crystal Growing

A total of seven samples were produced during the report period, identified as runs No. 12 through 18. Run No. 16 was for a special purpose, as noted below, and was not put through the Stockbarger furnace. In all cases, the Pb was held at about 700°C for one to three hours in a stream of hydrogen as the first step in the mixing process. This is to be compared with 400°C used previously. At the end of this time, the liquid Pb was allowed to run down into the quartz crucible where another heater winding kept is above the melting point. The Te was then melted and immediately allowed to run down into the crucible, where a partial reaction took place. Since the melting point of PbTe is considerably higher, the newly formed compound quickly solidified and prevented the rest of the constituents from mixing. The crucible was then allowed to cool to room temperature and was sealed off under either a vacuum or a partial pressure of hydrogen, as noted below.

The chief concern of the crystal growing work of this period was to achieve n-type material. All runs were made with 0.2% to 0.3% excess Pb, but the first four resulted in crystals that were p-type over the entire length with the exception of the top few mm. This is the last portion to solidify, and apparently contains a very large excess of Pb just before solidifying, since a cap of free Pb is always found on top of the crystal. Run No. 16 was a quickly solidified boule containing 0.3% excess Pb. It was, of course, polycrystalline, but it turned out to be n-type throughout. Run No. 17 was put through the Stockbarger furnace at a considerably higher dropping rate, and resulted in a nearly uniform single crystal that was n-type over better than half its length.

Run No 18 was made at an even faster dropping rate and was unsuccessful in that the boule was polycrystalline throughout.

3.3 Summary of Runs

Run No. 12. 0.2% excess Pb. Crucible sealed off in vacuum. PbTe melted and stirred for 3 hours. Transferred to Stockberger furnace, brought up to 950°C and held for 15 hours. Dropped through gradient at 3 mm/hr. Held at 850°C for 60 hours, reduced to room temperature over 8 hour period.

Uniform single crystal throughout. n-type for top few mm only. Resistivity 5×10^{-3} ohm-cm in p region.

Run No. 13. 0.2% excess Pb. Crucible sealed off in vacuum. Stirring and dropping rate as above. Held at 850°C for 68 hours, reduced to room temperature over 8 hour period.

Major part single crystal; evidence of two competing growth patterns near lower tip. n-type for top few mm only. Resistivity of p region 3×10^{-3} ohm-cm.

Run No. 14. 0.2% excess Pb. Crucible sealed off in small pressure of hydrogen (probably a few tenths of an atmosphere). Stirring and dropping rate as above. Held at 850°C for 24 hours, reduced to 500°C over 5 hour period; held at 500°C for 44 hours, reduced to room temperature over 8 hour period.

Top and bottom parts uniform single crystal, but center band contained unidentified irregularity. n-type for top few mm only. Resistivity of p region 5×10^{-3} ohm-cm.

Run No. 15. 0.2% excess Pb. Crucible sealed off in H_2. Stirring as above. Dropping rate 1.5 mm/hr. Instead of being held at 850°C for a long period, this sample was reduced to 600°C over a period of several hours, starting as soon as the crucible was entirely through the gradient. Held at 600°C for 48 hours, reduced to 450°C slowly; held at 450°C for 48 hours, reduced to room temperature slowly. This was first run using Te from all-glass purifying system, and using mixing apparatus with cold traps replacing drying towers.

Lower half contained two or more growth patterns, top half uniform single crystal. n-type top few mm only. Resistivity of p region 12×10^{-3} ohm-cm.

Run No. 16. 0.3% excess Pb. No attempt to grow single crystal.

PbTe formed and stirred for 2 hours, then held above melting point in vertical position for 15 hours. Crucible lifted out of furnace and cooled to room temperature quickly.

Boule polycrystalline throughout. n-type throughout. Resistivity 5×10^{-3} ohm-cm.

Run No. 17. 0.2% excess Pb. Crucible sealed off in H_2. PbTe formed and stirred for 3 hours. Dropping rate in Stockbarger furnace increased to 20 mm/hr. Temperature reduced from 850°C to 500°C over 7 hour period, held at 500°C for 11 hours, reduced to room temperature over 3 hour period.

Upper three-quarters of boule uniform single crystal, lower one-quarter somewhat irregular. n-type throughout more than half length of boule. Resistivity of n region 25×10^{-8} ohm-cm; resistivity of p region 5×10^{-3} ohm-cm.

Run No. 18. 0.2% excess Pb. Mixing and annealing essentially as in No. 17. Dropping rate increased to 29 mm/hr. This is first run with new supply of Pb.

Polycrystalline throughout.

3.4 Conclusions

From simple considerations, one would expect a PbTe crystal grown with excess Te to be p-type, and with excess Pb to be n-type. Earlier experience by British workers has indicated that the usual result of either condition is a p-type crystal, and they were able to achieve n-type material only by rigorously excluding oxygen.

Our experience, as summarized above, indicates that excluding oxygen is not enough, but that either the growth rate or the temperature and length of annealing, or perhaps both, must be adjusted properly. A possible explanation is that excess Pb tends to be excluded during the growth process, and that this exclusion becomes more complete for slower growth rates and for more extensive annealing. On the other hand, Run No. 18 appears to indicate that a single crystal will not be formed if the growth rate is increased beyond about 20 mm/hr. However, the possibility that our new supply of lead is causing some trouble has not as yet been ruled out.

Not much can be said as yet about the extent and influence of miscellaneous unknown impurities. It will be necessary to carry out conductivity and Hall effect measurements for many samples over a wide range of temperatures before some reasonable estimates can be made.

4. PLANS FOR THE NEXT INTERVAL

It is planned to continue the work along three broad lines. The present program of growing crystals will be continued with the purpose of producing n-type and p-type crystals at will, and later reducing the impurities At some point it will be appropriate to attempt to introduce known doping agents.

Electrical measurements of the conductivity and Hall effect will be undertaken over a sufficient range of temperatures and impurities to map out the field and relate the intrinsic and extrinsic regions.

Attempts will be made to produce a p-n junction and carry out measurements of interest.